PATENT COOPERATION TREATY

From the INTERNATIONAL BUREAU

PCT

NOTIFICATION OF ELECTION

(PCT Rule 61.2)

To:

Commissioner
US Department of Commerce
United States Patent and Trademark Office, PCT
2011 South Clark Place Room
CP2/5C24
Arlington, VA 22202
ETATS-UNIS D'AMERIQUE

in its capacity as elected Office

Date of mailing (day/month/year) 06 March 2001 (06.03.01)	
International application No. PCT/US00/16234	**Applicant's or agent's file reference** CL1446PCT
International filing date (day/month/year) 13 June 2000 (13.06.00)	**Priority date** (day/month/year) 17 June 1999 (17.06.99)
Applicant BIRCHENALL, Andrew, Kelsey	

1. The designated Office is hereby notified of its election made:

[X] in the demand filed with the International Preliminary Examining Authority on:

08 January 2001 (08.01.01)

[ ] in a notice effecting later election filed with the International Bureau on:

2. The election [X] was

[ ] was not

made before the expiration of 19 months from the priority date or, where Rule 32 applies, within the time limit under Rule 32.2(b).

The International Bureau of WIPO **34, chemin des Colombettes** **1211 Geneva 20, Switzerland**	Authorized officer Zakaria EL KHODARY
Facsimile No.: (41-22) 740.14.35	Telephone No.: (41-22) 338.83.38

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PCT PATENT RECORDS CENTER

From the
INTERNATIONAL PRELIMINARY EXAMINING AUTHORITY

To:

SIEGELL, Barbara, C.
E.I. du Pont de Nemours and Company
Legal Patent Records Center
1007 Market Street
Wilmington, DE 19898
ETATS-UNIS D'AMERIQUE

NOTIFICATION OF TRANSMITTAL OF THE INTERNATIONAL PRELIMINARY EXAMINATION REPORT
(PCT Rule 71.1)

Date of mailing *(day/month/year)*	25.09.2001
Applicant's or agent's file reference: CL1446PCT	**IMPORTANT NOTIFICATION**

International application No.	International filing date *(day/month/year)*	Priority date *(day/month/year)*
PCT/US00/16234	13/06/2000	17/06/1999

Applicant
E.I.DU PONT DE NEMOURS AND COMPANY

1. The applicant is hereby notified that this International Preliminary Examining Authority transmits herewith the international preliminary examination report and its annexes, if any, established on the international application.

2. A copy of the report and its annexes, if any, is being transmitted to the International Bureau for communication to all the elected Offices.

3. Where required by any of the elected Offices, the International Bureau will prepare an English translation of the report (but not of any annexes) and will transmit such translation to those Offices.

4. **REMINDER**

The applicant must enter the national phase before each elected Office by performing certain acts (filing translations and paying national fees) within 30 months from the priority date (or later in some Offices) (Article 39(1)) (see also the reminder sent by the International Bureau with Form PCT/IB/301).

Where a translation of the international application must be furnished to an elected Office, that translation must contain a translation of any annexes to the international preliminary examination report. It is the applicant's responsibility to prepare and furnish such translation directly to each elected Office concerned.

For further details on the applicable time limits and requirements of the elected Offices, see Volume II of the PCT Applicant's Guide.

Name and mailing address of the IPEA/	Authorized officer
European Patent Office D-80298 Munich Tel. +49 89 2399 - 0 Tx: 523656 epmu d Fax: +49 89 2399 - 4465	Ipinazar, P Tel.+49 89 2399-8131

REY NOTED

Form PCT/IPEA/416 (July 1992)

17 DE 2001

PATENT COOPERATION TREATY

PCT

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)

Applicant's or agent's file reference	FOR FURTHER ACTION	See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416)
CL1446PCT		
International application No.	International filing date *(day/month/year)*	Priority date *(day/month/year)*
PCT/US00/16234	13/06/2000	17/06/1999
International Patent Classification (IPC) or national classification and IPC D21H25/18		
Applicant E.I.DU PONT DE NEMOURS AND COMPANY		

1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.

2. This REPORT consists of a total of 6 sheets, including this cover sheet.

   ☒ This report is also accompanied by ANNEXES, i.e. sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).

   These annexes consist of a total of 6 sheets.

3. This report contains indications relating to the following items:

   - I ☒ Basis of the report
   - II ☐ Priority
   - III ☐ Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
   - IV ☐ Lack of unity of invention
   - V ☒ Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations suporting such statement
   - VI ☐ Certain documents cited
   - VII ☒ Certain defects in the international application
   - VIII ☒ Certain observations on the international application

Date of submission of the demand	Date of completion of this report
08/01/2001	25.09.2001
Name and mailing address of the international preliminary examining authority: European Patent Office D-80298 Munich Tel. +49 89 2399 - 0 Tx: 523656 epmu d Fax: +49 89 2399 - 4465	Authorized officer Naeslund, P Telephone No. +49 89 2399 8614

Form PCT/IPEA/409 (cover sheet) (January 1994)

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No. PCT/US00/16234

I. Basis of the report

1. With regard to the **elements** of the international application *(Replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to this report since they do not contain amendments (Rules 70.16 and 70.17))*:
Description, pages:

3,4	as originally filed			
1,2,2A,5,6	as received on	15/06/2001	with letter of	14/06/2001

Claims, No.:

1-10	as received on	15/06/2001	with letter of	14/06/2001

Drawings, sheets:

1/1	as originally filed

2. With regard to the **language**, all the elements marked above were available or furnished to this Authority in the language in which the international application was filed, unless otherwise indicated under this item.

   These elements were available or furnished to this Authority in the following language: , which is:

   - ☐ the language of a translation furnished for the purposes of the international search (under Rule 23.1(b)).
   - ☐ the language of publication of the international application (under Rule 48.3(b)).
   - ☐ the language of a translation furnished for the purposes of international preliminary examination (under Rule 55.2 and/or 55.3).

3. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international preliminary examination was carried out on the basis of the sequence listing:

   - ☐ contained in the international application in written form.
   - ☐ filed together with the international application in computer readable form.
   - ☐ furnished subsequently to this Authority in written form.
   - ☐ furnished subsequently to this Authority in computer readable form.
   - ☐ The statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.
   - ☐ The statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished.

4. The amendments have resulted in the cancellation of:

- ☐ the description, pages:
- ☐ the claims, Nos.:
- ☐ the drawings, sheets:

5. ☒ This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed (Rule 70.2(c)):

   (Any replacement sheet containing such amendments must be referred to under item 1 and annexed to this report.)
   see separate sheet

6. Additional observations, if necessary:

V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty (N)	Yes:	Claims	2-4,6-8
	No:	Claims	1,5,9,10
Inventive step (IS)	Yes:	Claims	NONE
	No:	Claims	1-10
Industrial applicability (IA)	Yes:	Claims	1-10
	No:	Claims	NONE

2. Citations and explanations
   see separate sheet

VII. Certain defects in the international application

The following defects in the form or contents of the international application have been noted:
see separate sheet

VIII. Certain observations on the international application

The following observations on the clarity of the claims, description, and drawings or on the question whether the claims are fully supported by the description, are made:
see separate sheet

Re Item I

Basis of the opinion

(i) Claims 1-8 (claims 2-4 by means of being dependent on claim 1) have been amended by means of a specification of the paper to be a "cellulosic" paper. Nowhere however in the original application documents is the term "cellulosic" used. While it can be agreed that papers are often to a great extent composed of cellulosic fibers there are however papers which also comprise to a main part, or as a whole, other fibers than cellulosic fibers (Art. 34(2)(b) PCT/Rule 70.2(c) PCT).

(ii) In claims 9 and 10 no basis for "pattern or printing" or "patterned or printed" article of paper or textile respectively can be seen. In relation to claim 9 it is further not seen where in the application as filed it was set out as optional that the textile substrate should be "fibrous", or that the amorphous fluoropolymer fibers should be interconnected (omission of essential features). Therefore these claims also comprise added subject-matter (Art. 34(2)(b) PCT/Rule 70.2(c) PCT).

Re Item V

Reasoned statement under Rule 66.2(a)(ii) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

Reference is made to the following documents:

D1: WO-A-92 10532
D2: GB-A-1 007 981
D3: US-A-5 409 736
D4: WO-A-97 19224

1. From D1 (see page 4, line 30-line 33; page 5, 2nd paragraph; claims 1,7-13, 21; examples 1,2) there is known a strengthened textile article comprising a fibrous textile substrate and amorphous fluoro polymer on the surface applied as a solution. Claim 9 therefore would not appear novel; Art. 33(2) PCT.

2. As to the process of claim 1, to the extent that it concerns a treatment of a textile

article it is not novel either in view of D1 (see example 1). The same is valid to claim 10 and claim 5.

3. I one embodiment claim 5 is related to a strengthened paper article. Starting from D1 however, it is generally known to the person skilled in the art that the feature "textile" is more or less an equivalent to the feature "paper" and that the boarder between these product categories is floating. See also the present application on page 3, paragraph 3. The skilled person would thus substitute textile for paper where circumstances make it desirable. This embodiment of claim 5 is therefore not inventive; Art. 33(3) PCT. Similar considerations apply to claims 1,9 and 10. Such a view is also supported by the teaching in D2 (see claims) as this document discloses the treatment of both paper and textile structures with compounds similar to those of D1, for strength. Therefore, also a combined reading of D1 and D2 by the skilled person deprives this embodiment of claim 5,1,9 and 10 of an inventive step; Art. 33(3) PCT.

4. Concerning the dependent claims they would at least not appear inventive in the light of the cited prior art, documents D3 (see claims) and D4 (see claims) inclusively. It is emphasized that even though these latter documents would address a different problem, to the extent that they teach the same process steps they are at least citable under novelty.

5. For the assessment of the present claims on the question whether they are industrially applicable, no particular reasoning would appear necessary to give. The industrial applicability would appear self evident (Art. 33(4) PCT).

NB. Also if one would consider that there is no added matter (cf. Item I-(i) and (ii) supra) in the present application (implicit disclosure of similar), an inventive step can in any case not be seen. Cellulosic papers and textile fabrics are similar in properties and behaviour. Both these types of material use to be patterned or printed.

Re Item VII

Certain defects in the international application

1. US-A-5 509 736 cited in the description should read US-A-5 409 736.

2. The two-part form ("characterized by"-form) should be applied to the independent claims over closest prior art.

3. The description should as far as national/regional legislation it so requires be adapted to any amended claims upon entry into the national/regional phase.

Re Item VIII

Certain observations on the international application

1. It is not clear from claim 1 (and also not from other independent claims) whether "cellulosic" also refer to the textile article (Art. 6 PCT).

TITLE

PRESERVATION OF PAPER AND TEXTILE MATERIALS

FIELD OF THE INVENTION

The present invention relates to the preservation of paper articles (e.g., books, manuscripts, documents) and textiles articles (e.g., paintings on canvas, clothing, etc.) through the application of an amorphous fluoropolymer by, for example, spraying, dipping or brushing the article to be preserved with a solution of the fluoropolymer.

BACKGROUND

Commonly owned and copending PCT International Application No. PCT/US98/26903 discloses coating a substrate (e.g., a metal, ceramic or composite) including the application of a fluoropolymer solution to seal pores.

The use of fluoropolymer dispersions to coat and protect paper and fabrics is known (see e.g., U.S. Patent Nos. 4,742,140 and 5,674,961). Generally, these dispersions are comprised of particles in the neighborhood of 80 to 400 nm in diameter in an aqueous medium. The particles are not intended to fully or uniformly coat the fibers of paper or fabric. Also, because they are generally aqueous dispersions, items containing water-soluble dyes would be damaged by contact with water.

WO A 92/10532 teaches fluorinating the surface of polymers by deposition of fluorocarbons from solution. WO A 97/19224 is a process for preserving paper by polymerizing polycondensates *in situ*. GB A 007 981 discloses lamination of paper or textile articles. US 5,509,736 describes impregation of paper with particles of oxides which hydrate to bases.

SUMMARY OF THE INVENTION

The present invention provides a method for strengthening a cellulosic paper or textile article, comprising the steps of (a) applying to the article a solution of an amorphous fluoropolymer in a perfluoroalkane solvent; and (b) drying the article so that the solvent is essentially removed.

The present invention also relates to a strengthened cellulosic paper or textile article comprising (i) a fibrous cellulosic paper or textile substrate and (ii) amorphous fluoropolymer interconnecting fibers of said substrate.

BRIEF DESCRIPTION OF THE DRAWING

Figure 1 represents a plot of data from Table 1.

DETAILED DESCRIPTION

The present invention employs amorphous fluoropolymers which, for application, are dissolved in a perfluoroalkane solvent. Articles to be preserved are treated with the fluoropolymer solution by any suitable method, including but

not limited to dipping, spraying and brushing. The article may be, but is not limited to, a book, manuscript, paper, fabric, article of clothing, painting, and the like. Normally, the amorphous fluoropolymer is used substantially transparent, and consequently there is no substantial difference in appearance between the treated article and the untreated article.

When fluoropolymer is deposited from solution onto a non-porous surface, a coating of about 5 to 20 μm thick typically results. This thickness is related to the concentration of the solution used in the deposition. Generally, a 1% solution will produce a film about 5 μm thick, and a 6% solution yields a film thickness of about 50 μm. However, when the object on which the fluoropolymer is deposited is fibrous or porous, the fluoropolymer penetrates into the object. Commonly owned and copending PCT International Application No. PCT/US98/26903 and U.S. Patent Application Serial No. 215,441 describe the penetration of fluoropolymer solutions into pores in thermal spray coatings which are used for corrosion protection. Fluorine x-ray fluorescence micrographs were used to demonstrate fluoropolymer penetration into the pores.

Useful herein are solutions of fluoropolymers with molecular weights in the range of from 200,000 to 400,000. These fluoropolymers are known to have excellent chemical resistance; and their solutions generally have relatively low viscosities, on the order of about 0.060-0.300 pascal seconds (60 to 300 centipoise) at shear rates from about 50 to 300 sec^{-1}, which enables them to flow into the pores. The location of the fluoropolymer in the pores is also important because, unlike purely surface films, the material is not easily abraded or worn away. Rather, the fluoropolymer in the pore is protected from abrasion by the surrounding porous coating as well as any surface coating. Moreover, the fibers of the substrate are interconnected with fluoropolymer, thereby strengthening the article.

Treating paper with fluoropolymer solutions can significantly increase the tensile strength of paper, as shown in Example 2 below, as well as typically impart other desirable properties. The films or deposits have very low surface energies compared to untreated paper (e.g., in the range of 15 to 19 dynes/cm). Thus, they are generally difficult to wet with liquids such as water. Solid deposits like dirt, dust or inks will not easily adhere to such surfaces. The permeation of aggressive chemical constituents of the environment which may degrade or corrode the object is retarded, as the solutions penetrate into the bulk of the material as well as depositing on the surface. Finally, the fluoropolymer film or deposit itself is very inert to degradation from environmental chemicals.

One use for this invention is the preservation of a variety of papers, including books, newspaper pages and documents. As paper ages, it frequently becomes more brittle. This is a problem for historic books and documents of great age. Treatment of these papers with the fluoropolymer solutions, as described in this invention, have been shown to increase the tensile strength of the paper, as shown in the Examples below. As outlined in Examples 1 and 2 below, a paper or book can be dipped into the fluoropolymer/perfluoroalkane solution and air dried

Minneapolis, MN). In general, the perfluoroalkane solvents used in these solutions are not considered aggressive to many paper and textile articles. Most inks will not dissolve in perfluorinated solvents. Similarly, many substrates are unaffected by exposure to these solvents.

The fluoropolymer solutions may be applied to the fibrous articles by common coating methods, including but not limited to spray application, dipping and brushing. After application of the solutions, the articles can be dried by conventional methods (e.g., air or vacuum drying).

EXAMPLES

Fluoropolymer Solution Preparation:

Teflon® AF solutions were used in the examples below, and were used as received from E. I. du Pont de Nemours and Company, Wilmington, DE, unless otherwise noted. To dilute the Teflon® AF2130, solvent (FC-75, 3M, Minneapolis, MN) was weighed and was placed into a container, with the calculated amount of Teflon® AF2130 added to the solvent. The samples were mixed before use.

EXAMPLE 1

Paper Treatment

Several types of paper, including newsprint and copier paper were dipped for about 30 seconds into several Teflon® AF solutions, having concentrations between 1 and 6% solids by weight, such that about half the sheet was impregnated with the solution. The papers were removed from the solution and dried for about 30 minutes. The entire sheets of paper were immersed in water at room temperature. The treated portion emerged in undamaged condition while the untreated paper fell apart. No dissolution or blurring of ink was observed in the treated portion of the newsprint.

EXAMPLE 2

Strength Testing of Paper

The strength of treated paper was compared to that of an untreated paper. Strips of paper (20 pound White Wove, Gilbert, Inc., Menasha, WI) about 2.5 cm (1 inch) wide, 20.3 cm (8 inches) long, and 0.010 cm (0.004 inches) thick, were immersed for 10 minutes in solutions with varying concentrations of fluoropolymer. The strips were removed and dried, leaving a fluoropolymer deposit in the paper. The tensile strengths of the strips were measured using a model 1122 Instron test machine (Instron Corp., Canton, MA) and ASTM Method D 828 procedures (the test bars were held in grips with a separation of 5 inches, and the cross head speed was 2 inches/minute). The fluoropolymer treatment

increased the strength of the paper. The results are shown in Table 1 below, as well as in Figure 1.

TABLE 1

Fluoropolymer Solution Identification	Concentration of Fluoropolymer, %	MPa	Strength, Ksi	% Increase in Strength vs. Control
None	0	44.0	6.38	---
TEFLON® AF1600	3	51.2	7.42	16.3
TEFLON® AF1601	6	56.1	8.14	27.6
TEFLON® AF2400	1	48.9	7.09	11.1
TEFLON® AF2130	6	59.3	8.60	34.8
TEFLON® AF2130	3	59.0	8.55	34.0
TEFLON® AF2130	1	47.8	6.94	8.8

CLAIMS

What is claimed is:

1. A method for strengthening a cellulosic paper or textile article, comprising the steps of:

(a) applying to the article a solution of an amorphous fluoropolymer in a perfluoroalkane solvent; and

(b) drying the article so that the solvent is essentially removed.

2. The method of Claim 1 wherein the fluoropolymer has a molecular weight in the range of from 200,000 to 400,000.

3. The method of Claim 1 wherein the fluoropolymer is a copolymer of 4,5-difluoro-2,2-bis(trifluoromethyl)-1,3-dioxole with either tetrafluoroethylene or chlorotrifluoroethylene.

4. The method of Claim 1 wherein the fluoropolymer is a copolymer of tetrafluoroethylene with a monomer selected from fluoroolefins having from 2 to 8 carbon atoms and fluorinated alkyl vinyl ethers where the alkyl group contains from 1 to 5 carbons.

5. A strengthened cellulosic paper or textile article, comprising:

(i) a fibrous cellulosic paper or textile substrate; and

(ii) amorphous fluoropolymer interconnecting fibers of said substrate.

6. The strengthened cellulosic paper or textile article of Claim 5 wherein the fluoropolymer has a molecular weight in the range of from 200,000 to 400,000.

7. The strengthened cellulosic paper or textile article of Claim 5 wherein the fluoropolymer is a copolymer of 4,5-difluoro-2,2-bis(trifluoromethyl)-1,3-dioxole with either tetrafluoroethylene or chlorotrifluoroethylene.

8. The strengthened cellulosic paper or textile article of Claim 5 wherein the fluoropolymer is a copolymer of tetrafluoroethylene with a monomer selected from fluoroolefins having from 2 to 8 carbon atoms and fluorinated alkyl vinyl ethers where the alkyl group contains from 1 to 5 carbons.

9. A strengthened article of paper or textile, comprising:

a) a pattern or printing, and

b) an amorphous fluoropolymer coating applied from an amorphous fluoropolymer solution such that the information conveyed by the pattern or printing is not obscured or distorted.

10. The process of treating a patterned or printed article of paper or textile comprising: applying to the article a solution of an amorphous fluoropolymer in a perfluoroalkane solvent; and drying the article so that the solvent is essentially removed.